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Electro-Deposition of Brass

Elec. Engineering
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ELECTRO-DEPOSITION OF BRASS

BY

LEONARD JOHN LEASE

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

ELECTRICAL ENGINEERING

IN THE

COLLEGE OF ENGINEERING

UNIVERSITY OF ILLINOIS

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May 27, 1904 190

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

LEONARD JOHN LEASE

ENTITLED ELECTRODEPOSITION OF BRASS

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor of Science in Electrical Engineering

Morgan Brooks

HEAD OF DEPARTMENT OF Electrical Engineering.

CONTENTS.

INTRODUCTION.

There are several ways of ontaining a thin coating of brass on cheaper metals as iron rods, fixtures, piping, railing, etc., but not all of the methods are applicable to all of the different objects to be plated. The objects may be coated with alternate layers of copper and zinc and alloyed by heating, iron rods may be placed in a thin hollow tubing of brass and drawn into rods or wire, or a thin coating of brass may be obtained electrolytically. This seems to be the only method applicable to all the objects to be plated. The inside of hollow objects or cups can be plated by placing the solution in the cup and suspending an anode into the solution and using the object as cathode. Anodes of copper and zinc were tried by the author and found to be a success.

HISTORIC.

The early brass plating was done by depositing a layer of copper and one of zinc separately and after cleaning and drying was heated just sufficiently to cause the two metals to alloy superficially. With small or odd shaped pieces of metal this heating necessary to produce the alloy, was injurious to the objects plated, causing them to loose their shapes or melting them entirely when made of low melting metals. Brass plating by electrolysis was first made about 1841 and seemed to be the result of efforts to overcome this difficulty.

In the preparation of electrolytic baths the three principle methods used were to dissolve chipped brass in acid, to dissolve the brass electrolytically and to prepare the solutions from salts of copper and zinc. By dissolving the brass in acid a bath containing the metals in the same proportions as the desired deposit was obtained. An excess of brass was always used to prevent the solution from becoming acid. The filtered or decanted solution was then diluted to two or three times its volume, aqueous ammonium added until the solution became a deep blue and just sufficient potassium cyanide was added to clear up the solution. A little cyanide was occasionally added during deposition to clean the electrodes. By electrolysis the bath was prepared by passing a current through a suitable solution(not mentioned) from a brass anode, so that the alloy dissolves simultaneously in the liquid and gives a bath of the same proportions of copper and zinc as the anode. Or a copper anode was placed in the bath and a current passed through it until the solution was well saturated with copper, then a zinc anode was

substituted and a current passed through this until the proper brass color was obtained on the cathode, when a brass anode was placed in the bath instead of the zinc. The solutions made from the salts of the metals is the modern method and the one employed by the present platers of brass. The formulae are entirely empirical and may be varied considerably. The one most used in practice and the one employed in these experiments being Roseleur's and consisted of the following per liter:

10 grams $NaHCO_3$.

14 " $NaHSO_3$.

14 " $Cu(C_2H_3O_2)_2$.

14 " $ZnCl_2$ fused.

40 " KCN.

2 " NH_4Cl.

To prepare this bath the sodium acid carbonate was dissolved in twenty times its volume of water at fifty degrees centigrade and the sodium acid sulphite added in small quantities, to prevent too vigorous effervescence. With this was mixed the copper acetate and zinc chloride solution formed by dissolving these salts in ten volumes of boiling water. The potassium cyanide was dissolved in a small quantity of water and added to the above until the blue color disappeared. If the cyanide was not pure more would be necessary. After dissolving the ammonium chloride and adding it, the whole was made up to one liter and ready for use.

GENERAL PRINCIPLES.

Brass plating while perfectly practical is much more difficult to accomplish satisfactorily than to deposit a single metal. A brass bath is considered as a mixture of copper cyanide and zinc cyanide or may be a complex salt of copper-zinc-cyanide in a suitable solvent.

A solution of copper cyanide requires a different current strength from a solution of zinc cyanide. One author states that the current is required to force zinc out of solution and copper into solution. The current reduced sufficiently will deposit copper alone or if increased sufficiently will deposit zinc alone. The less positive metal deposits first thus copper being negative with respect to zinc will tend to go out of solution first; this may be seen when a strip of zinc is dipped into the bath, the copper at once separates on the zinc giving it a bright copper appearance.

The solutions recommended by Roseleur and used extensively by Pfanhauser contained equal quantities of copper and zinc with the addition of carbonates and sulphates or some other similar salts. These aid in giving the solution a greater conductivity and may help to keep the electrodes clean. Arsenious acid in small quantities gives a bright color to the brass but when present in too large quantities gives a pale color.

All the solutions require the addition of copper and zinc cyanide after being worked for some time as a weak solution will not deposit brass. Copper being used in larger quantities in the deposit has to be replenished first.

The anode surface should be about twice that of the cathode.

It is claimed that the nature of the deposit may be regulated by the amount of anode surface exposed. More anode surface gives a larger percentage of zinc, less surface gives more copper.

If the anodes do not clean after running for some time, and become slimy and black, more cyanide should be added, also a little ammonium hydroxide. This tends to prevent a white salt of zinc from depositing on the anode. Too much cyanide may make the metal deposit slowly or not at all or may cause the deposit to blacken on the cathode and bubbles form very rapidly.

The early platers boiled their solutions for an hour or two or forced the current through the solutions for twenty to twenty-five hours before starting to plate with it. Pfanhauser claimed that this is not necessary but in the tests used in this work the first deposits obtained showed red spots of copper which became smaller and finally disappeared after the solution was used for four or five hours. All solutions should be stirred well to prevent the solution around the cathode from becoming metal poor and the deposit uneven.

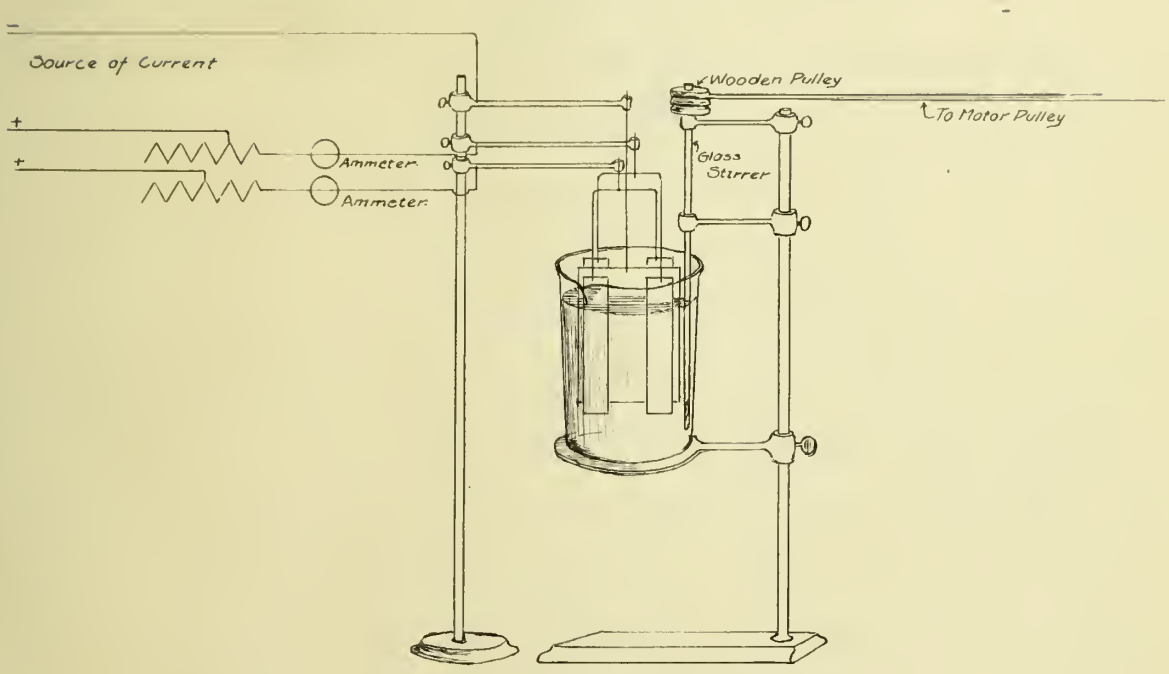
DEPOSITION OF BRASS.

In this experimental work Roseleur's solution was employed. About 300 c c were placed in a 500 c c beaker and in this was suspended the platinum cathode with a surface of 50 square centimeters between the two anodes of brass. In a series of experiments the brass anodes were replaced by copper and zinc electrodes. The depositions were carried on in one hour runs. The runs were made at different temperatures and current densities to determine the best conditions for plating.

The solution was agitated by means of a glass rod, flattened and twisted at one end forming a screw and rotated by a belt from a small 110 volt motor. The rod had two bearings of glass tubing about one inch long and just large enough to permit the rod to pass through. The belt pulley, made of wood, rested on the top of the upper bearing forming the support. The bearings were held by clamps on a ring stand.

After the solution had been used for six to eight runs the anodes became black and slimy.. About two grains of cyanide and eight to ten drops of ammonia cleaned them and the deposition was much improved. In one case too much cyanide was added and the cathode showed black spots and nearly half of one side showed a black deposit. When placed in acid this disappeared at once leaving a red coating of copper between the black and the platinum electrode. This would indicate the black deposit to have been a crude coating of zinc.

Brass Depositing Apparatus.

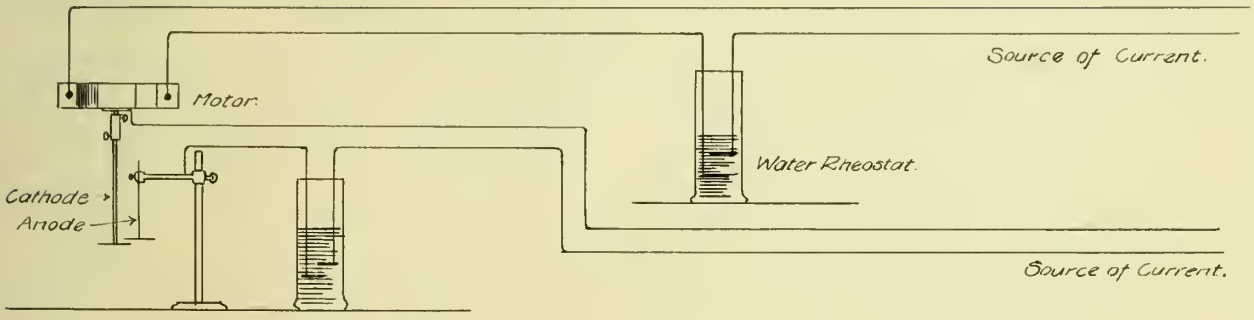


ANALYSIS OF DEPOSITED BRASS.

The determination of the percentage of copper and zinc in the deposited brass was obtained by dissolving the brass in nitric acid and separating the copper from the solution electrolytically. Separation of copper from a nitric acid solution by the ordinary method of anode and cathode dipped into the solution was too slow for the determinations of the copper in the brass, so a rotating cathode was tried. The first form used and which gave good results was to rotate a small platinum crucible by means of a vertical shaft belted to a 110 volt motor. The crucible was fastened to the shaft by a rubber stopper, and electric connection made with lamp cord soldered into the end of the shaft projecting into the crucible. On account of the stopper being soft and elastic the speed could not be raised high enough for rapid depositions. Separation could be made in forty to fifty minutes. The second and seemingly the most satisfactory method was to use an ordinary disc electrode as cathode. This was rotated by a small toy motor. The cathode was connected to the motor shaft by a brass connector and the electric connection to the cathode made through the frame of the machine. The cathode hung free and rotated about its own center of gravity. As long as the motor kept its speed the cathode rotated smoothly but a sudden decrease in its speed would throw the cathode off center, causing it to strike the side of the beaker or anode and thus scratch off the deposit and possibly breaking the beaker.

In this work the brass was dissolved in as small an amount of hot nitric acid as would dissolve it in a few minutes and about three cubic centimeters concentrated sulphuric acid and the whole

COPPER SEPARATING APPARATUS.



diluted to about 250 c c. This gave good results and in less time than in nitric acid solution. A current of five amperes normal density was used in all three separations. The end of the separation was indicated by placing a drop of the solution in dilute potassium-ferro-cyanide, if no red tints could be seen the separation was complete.

The weight of the brass dissolved being known, and the weight of the copper found by the above separation, the amount of zinc which was left in solution was calculated, since no other metal was present. As zinc cannot be separated from nitric acid solution the electrolytic determination was not attempted on account of the time required to evaporate the nitric acid from the solution, from which the copper had been separated.

POTENTIAL MEASUREMENTS.

The solution tension between the brassing solution and the electrodes was measured by the fall of potential method. A zero method was used and the Lippmann's electrometer was used as zero indicator. The apparatus used in these measurements consisted of a Standard Resistance box, Lippmann's electrometer, a normal electrode, two Laclanche cells and a contact key. The standard resistance consisted of a box of 1000 ohms divided into 9 of 100 ohmes each and 10 of 10 ohms each as shown in diagram. Potentials above that of the cells,c, were measured by placing a standard cell or two against the unknown potential and balancing the difference on the standard resistance box. Let E be the e. m. f. of cells,C, Ex that of the system B, N or the unknown then E :E ::1000:R, R being the reading of the box.

The electrometer may be said to be the most important part of the apparatus. The electrometer proper consists of a capillary tube between two tubes A and B as shown. Mercury is placed in tube A and sulphuric acid (10% sol.) in tube B. Several drops of mercury are blown through the capillary into tube B and when the mercury is drawn back into the capillary the acid follows. The working of the electrometer is based upon the fact that the surface tension of mercury in contact with an electrolyte (dilute sulphuric acid) changes when the difference of potential at the point of contact changes. The two quantities of mercury are connected by the sulphuric acid, one having a large surface in contact and the other a small one; when a change in the potential occurs between the two, the disturbance is in proportion to their exposed surface or effects

the small one almost exclusively. This a difference of potential disturbs the equilibrium of the capillary mercury and causes it travel up or down depending upon the direction of the pressure. The movement of the mercury is very slight for small differences of potential and must be read with a microscope. The electrometer is mounted in front of a microscope by an arm from the microscope stand and a mirror held behind the electrometer by another arm from the same, giving a bright field at the capillary. The microscope contains a scale and by the use of this potentials of 0.001 volt can be measured.

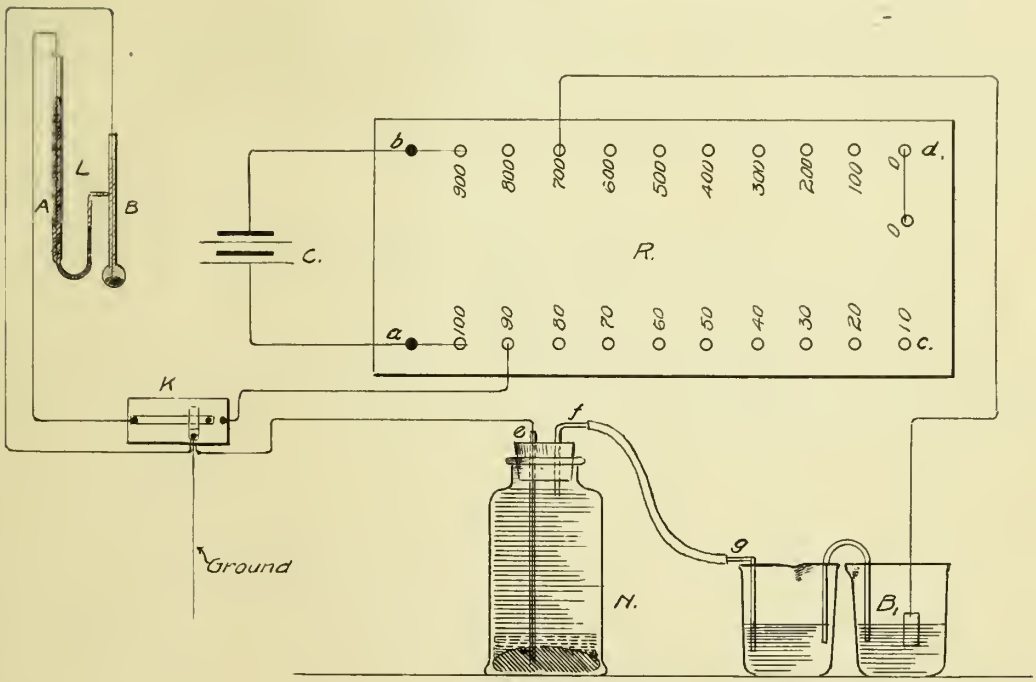
To make potential measurements between electrode andelectrolyte at least one more electrode and usually another electrolyte is necessary. For the purpose the normal electrode is used. This is made by covering the bottom of a bottle with pure mercury, adding a layer of mercurous chloride and filling the bottle with a solution of normal potassium chloride. The completely filled bottle is stopped and sealed with a rubber stopper bearing two tubes as shown at M. The tube e has a small platinum wire sealed in the bottom end and by placing a drop of mercury in the tube electric connection is made with the mercury in the bottle. The other tube just extends through the stopper and to it is attached a piece of rubber tubing which is provided with a bent glass tube and the whole filled with normal potassium chloride solution.

The cells used were ordinary zinc-carbon in salammoniac.

The contact key was of special design closing the circuit through the electrometer when opening the main circuit. This was to prevent capacity effect in the electrometer.

In making the measurements for this work the normal electrode

POTENTIAL MEASUREMENT APPARATUS.



was used, the free end dipping into a beaker of normal potassium chloride and contact with the brassing solution in the second beaker by use of a syphon filled with normal potassium chloride. Two cells were used to bring the electromotive force between a and b above the algebraic sum of the potentials of the normal electrode and that between the brassing solution and the metals. The e. m. f. between brass, zinc or copper and the solution is positive with respect to mercury and its electrolyte so the e. m. f. of the normal electrode which is -0.56 volt is added to the calculated value to obtain the e. m. f. between the bath and metals. Let E_c be the pressure of the system B H, E that of the normal electrode, or -.56, E_x that of the unknown.

$$E_c = E_x - E_a, \quad E_x = E_c + E_a = E_c - 0.56.$$

In connecting up the apparatus the mercury, or B, of the electrometer, must be connected with the same circuit as the zinc in the battery.

DATA AND RESULTS.

Table 1 shows the result of running a bath at room temperature for six one-hour runs. The bath was made up according to Roseleur's formula (page 2 above) and the deposition started without any heating or working through with the current. The first deposits were not satisfactory, large red spots of copper appearing which disappeared entirely in the third run and the remainder of the deposits were good, some showing a crystaline appearance. This run showed that there was no appreciable deterioration of the bath. The amount of deposited brass was not constant, showing that the results do not duplicate readily. The variation may be due to fluctuations in the storage battery current, or a constant changing of resistance in the plating cell. The potential between the brass anode and bath changes irregularily but that between clean strips of copper and zinc and the bath show a gradual increase. The irregularity of the brass anode measurements were probably due to a shiny coating on the brass, as the measurements were made on the anode without cleaning it.

Table 2 shows a series of experiments made by varying the current density, at constant temperature for a series of different temperatures. The same bath was used as in Table 1. At the end of the run at 25°, about a gram of cyanide and ten to twelve drops of ammonium were added. This cleaned the anodes and brightened the deposited brass. In this set of experiments two sets of apparatus were used and the solution in the two beakers well mixed with each other at the end of each run. This would tend to keep the conditions the same in both baths. At the end of the 40° run

about 100 c c of new solution were added after removing about the same amount of the old solution. At the higher temperatures the water vaporized from the bath, so distilled water was added frequently to keep the solution of the same density. In these experiments the solution tention of the deposited brass was measured and in most of the runs show an increase. The brass anode shows about the same irregularity as in Table 1. The copper separations show that as the current density is increased the proportion of copper in the deposited brass increases. Temperature does not seem to affect the percentage of copper and zinc appreciably.

In Table 3 a new bath was taken and a run made at different current densities at 500 C. with zinc and copper anodes. The same was tried on the bath used in Table 2, starting at 0.2 ampere. In this the zinc was soon covered with a coating of copper. At the end of the run the copper was taken off with nitric acid and 0.3 and 0.4 amperes tried. By this time the bath had lost so much zinc that the cathode showed a crude coating of copper. The new bath was tried starting at 0.3 ampere. The zinc coated with copper on the side away from the cathode, but not appreciably on the inside so the current density was raised and when 0.5 ampere was reached no copper appeared on the zinc,and from this to 1.2 ampere the zinc remained clean. The deposited brass showed a good color as high as the current densities were carried, but it seemed to blister and deposit in bumps at from 0.9 to 1.2 amperes. The potential measurements were not made on this set of experiments as it was taken to determine the conditions preliminary to the final set of data which could not be done, on account of the armature of the 110 volt dynamo breaking down.

TABLE I.

A.

DEPOSITION OF BRASS.

I.	Temp. Deg. C.	Anode Loss	Cathode Gain.	Loss / Gain.	Theo. Deposit.	Current Eff.
3	25	0.160	0.248	0.645	0.359	69
"	"	0.141	0.244	0.573	"	68
"	"	0.035	0.274	0.123	"	76
"	"	0.257	0.208	1.236	"	58
"	"	0.209	0.250	0.836	"	70
"	"	0.166	0.266	0.624	"	78

C

SINGLE POTENTIAL MEASUREMENTS.

I.	Brass	Copper	Zinc.	Temp. Deg. C.
3	.26	.25	.49	25
"	.41		.50	"
"	.43	32	.51	"
"	.43	.36	.56	"
"	-.41	.35	.38	"

TABLE 2.

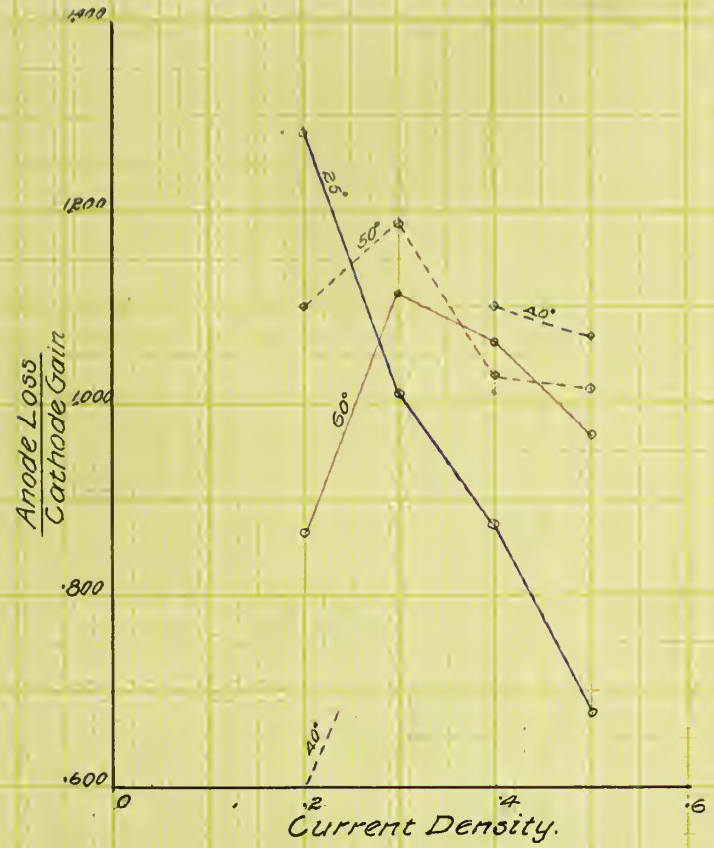
A.

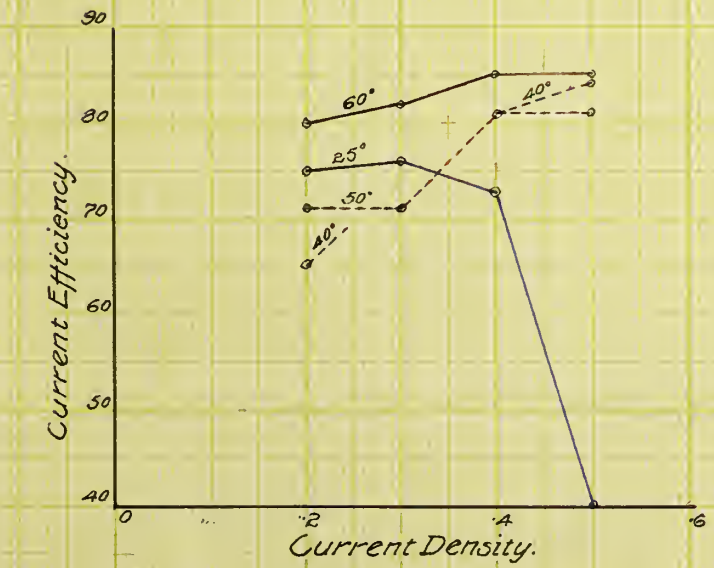
DEPOSITION OF BRASS.

I	Temp. Deg. C.	Anode Loss	Cathode. Gain.	Loss / Gain.	Theo. Deposit.	Current Eff.
0.2	25	0.232	0.181	1.282	0.239	75
0.3	"	0.275	0.272	1.011	0.359	76
0.4	"	0.304	0.348	0.874	0.479	73
0.5	"	0.163	0.241	0.676	0.598	40
0.2	40	0.094	0.155	0.604	0.239	65
0.3	"					
0.4	"	0.425	0.386	1.101	0.479	81
0.5	"	0.536	0.502	1.069	0.598	84
0.2	50	0.182	0.171	1.063	0.239	71
0.3	"	0.291	0.254	1.114	0.359	71
0.4	"	0.409	0.386	1.061	0.479	81
0.5	"	0.469	0.485	0.967	0.598	81
0.2	60	0.269	0.192	1.100	0.239	80
0.3	"	0.351	0.295	1.189	0.359	82
0.4	"	0.418	0.406	1.029	0.479	85
0.5	"	0.513	0.507	1.012	0.598	85

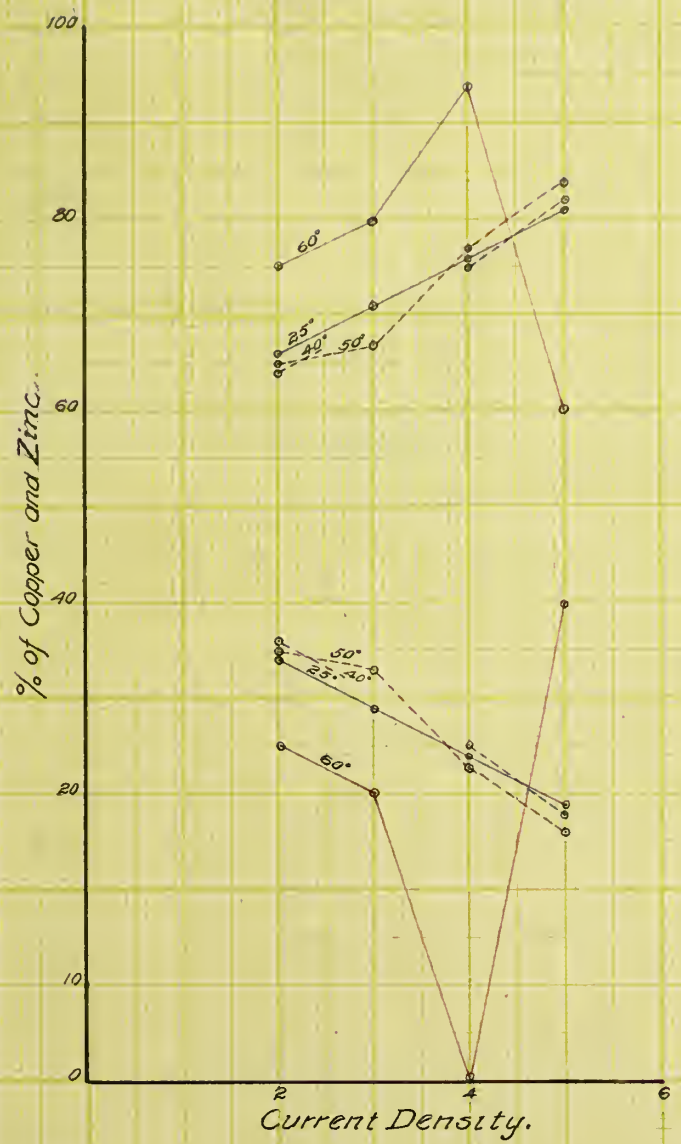
TABLE 2.

B. SEPARATION OF COPPER AND ZINC.					C. SINGLE POTENTIAL MEASUREMENTS.			
Copper	Zinc	% Copper	% Zinc	25° L.	Brass	Copper	Zinc	Deposited Brass.
0.119	0.062	66	34	0.2	0.18	0.32	0.62	0.35
0.194	0.078	71	29	0.3	0.16	0.40	0.64	0.42
0.265	0.083	76	24	0.4	0.33	0.33	0.64	0.42
0.193	0.046	81	19	0.5	0.33	0.40	0.64	0.47
				40°				
0.100	0.055	64	36	0.2	0.54	0.59	0.65	0.62
				0.3				
0.292	0.094	75	25	0.4	0.33	0.42	0.64	0.43
0.422	0.079	82	18	0.5	0.32	0.39	0.64	0.43
				50°				
0.111	0.060	65	35	0.2	0.17	0.49	0.68	0.54
0.179	0.082	67	33	0.3	0.12	0.49	0.67	0.54
0.301	0.085	77	23	0.4	0.18	0.40	0.63	0.44
0.408	0.078	84	16	0.5	0.31	0.39	0.63	0.44
				60°				
0.144	0.048	75	25	0.2	0.46	0.49	0.48	0.52
0.236	0.073	80	20	0.3	0.28	0.47	0.70	0.52
0.383	0.023	94	06	0.4	0.41	0.52	0.72	0.55
0.307	0.100	60	40	0.5	0.48	0.52	0.73	0.57

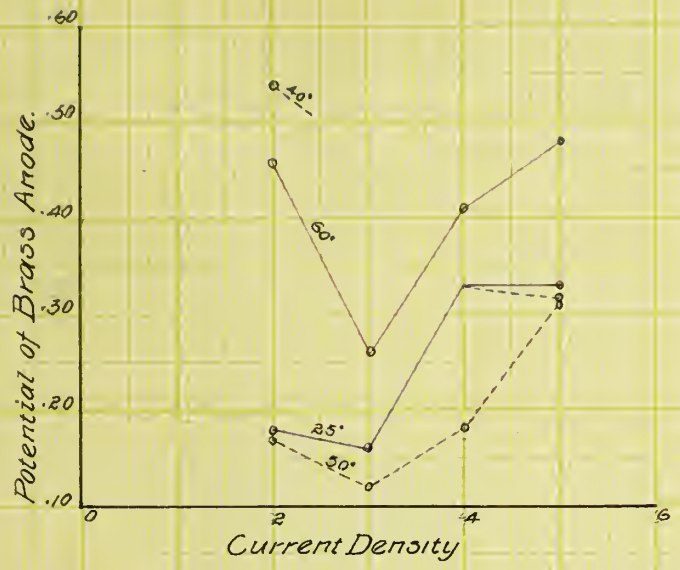


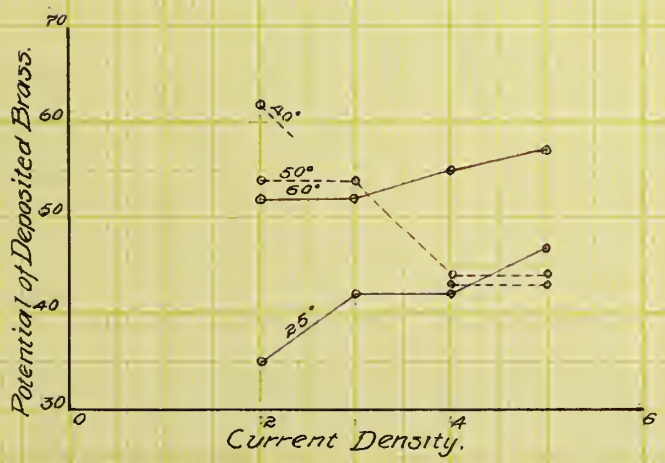


Curves from Table 2A.
Deposition of Brass.

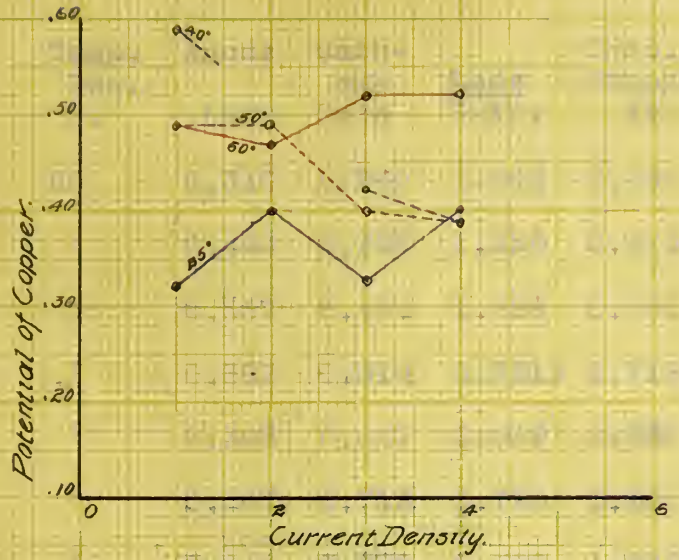


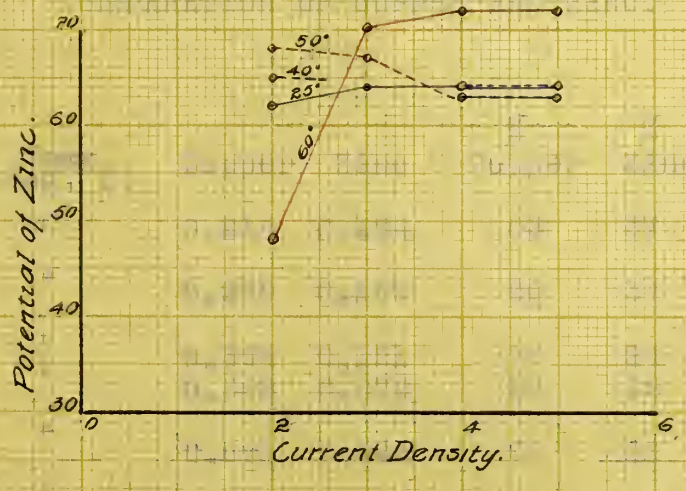
Curves from Table 2B
Copper Separation.





Curves from Table 20.
Potential Measurements





Curves from Table 2C
Potential Measurements

TABLE 3.

A.

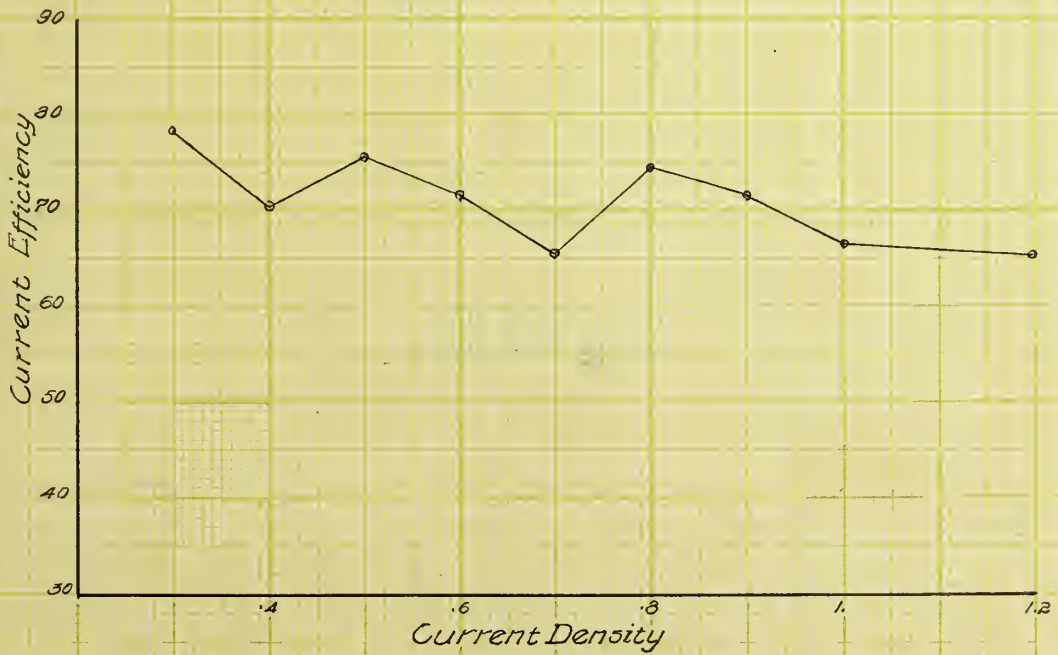
DEPOSITION OF BRASS.

I.	Temp. Deg. C.	Anode Loss	Cathode Gain	Loss Gain.	Theo. Deposit.	Current. Eff.
.3	50	0.310	0.246	1.262	0.359	68.5
.4	"	0.423	0.338	1.250	0.479	70.5
.5	"	0.557	0.454	1.228	0.598	75.8
.6	"	0.387	0.514	0.7515	0.718	71.6
.7	"	0.368	0.647	0.569	0.838	65.3
.8	"	0.567	0.713	0.795	0.958	74.5
.9	"	0.616	0.772	0.798	1.078	71.6
1.0	"	0.693	0.797	0.870	1.197	66.6
1.2	"	0.681	0.936	0.727	1.436	65.2

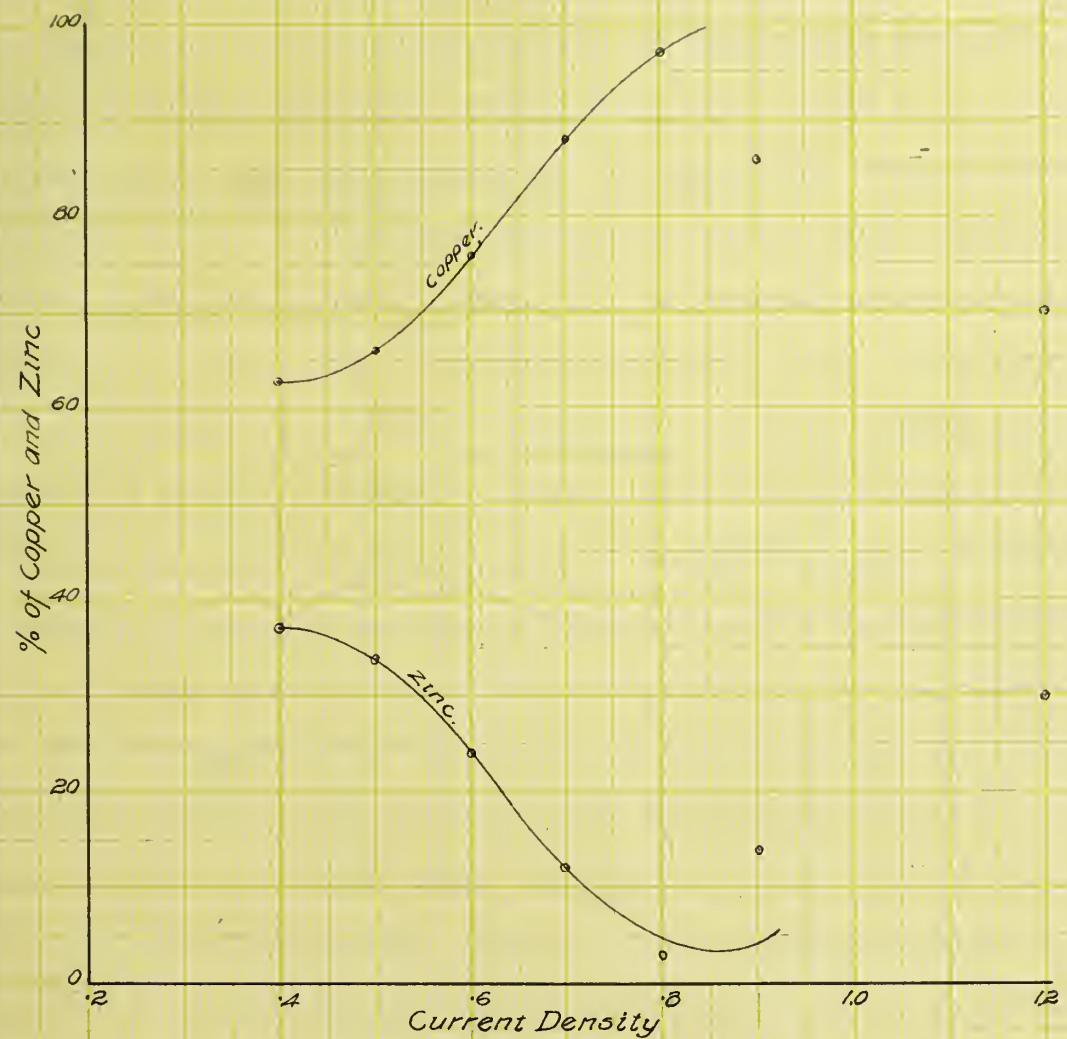
B.

I. SEPARATION OF COPPER AND ZINC.

I.	Temp. Deg. C.	Copper	Zinc	% Copper	% Zinc.
.4	50	0.214	0.124	63	37
.5	"	0.299	0.155	66	34
.6	"	0.394	0.121	76	24
.7	"	0.568	0.079	88	12
.8	"	0.691	0.042	97	03
.9	"	0.646	0.126	86	14
1.0	"		Lost.		
1.2	"	0.653	0.284	70	30



Curves from Table 3A.
Deposition of Brass.



Curves from Table 3B
Separation of Copper and Zinc.

CONCLUSION.

These experiments show that while the percentage of copper and zinc cannot be controlled entirely by the current density, it may be controlled closely enough to obtain a good adherent deposit of brass for ordinary work. Contrary to Pfanhauser's statement and also of other experimenters, it was found that a good looking brass can be deposited electrolytically at current densities as high as 1.2 amperes normal density. The temperature effects the current efficiency more than the nature of the deposited brass. The experiments show that the changing conditions in the bath itself effects the percentage of copper and zinc in the deposit much more than the temperature. This shows that it is necessary for copper and zinc salts to be added to the bath from time to time to keep conditions the same and obtain a uniform brass. This is also shown in Table 3, Section A, under anode loss divided by cathode gain. In the first experiments the anode loss was greater than the cathode gain, but soon fell below and continued below throughout the experiment.

Table 3 shows that the zinc and copper anodes may easily be substituted for the brass but require more attention. The current density in the copper and zinc anodes may be determined partly by the percentage of copper and zinc in the deposited brass, but when a white salt of zinc appears on the zinc anode the current must be reduced through it and increased through the copper.